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Lithium deposition on high energy irradiated LiF crystals

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Lithium metallic colloids were studied in ion-implanted LiF crystals, irradiated with high energy He^+ particles. The presence of metallic particles, displaying absorption bands at 420 and 460 nm due to the scattering of light on these particles, overlaps the absorption of M centers. The luminescence excited in this band, which is a superposition between the absorption of F_2 and F_3^+ centers, is reduced due to the metallic lithium particles, formed on the surface of the irradiated and at the end of the tracks of He^+ particles, reducing the luminescence of the formed color centers. Diminution of the M band together with the growing of the 420 nm band versus irradiation doses, suggest a transformation of the color centers in small F_n-aggregates during the irradiation process, followed by a metallic conversion of Li ions.

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1. Introduction

One of the promising next steps from the theoretical study to practical applications seems to be LiF material. Based on the color centers, LiF can be used in the practical applications like: distributed feed-back laser [1], micro-cavities [2] or micro-radiography [3]. The color centers used in such devices are the common F_2 and F_3^+ centers produced by low energy electron irradiation, high energy alpha electrons particles or and with soft X-ray plasma source.

Many papers are devoted to the irradiation with high energy beams (MeV electrons, He^+ ions, H^+ ions, Li^+ ions) which produce color centers in the bulk and the surfaces were practically neglected. For high irradiation doses (over 100 Mrad), metallic particles are formed, which are distributed heterogeneously on the crystals [1,2]. The interaction of ionizing particles with the lattice is done by the ion-implants in the thin layer from the surface. The mechanism consists on the increasing of the F centers in the initial part of the tracks, together with an increasing of the refractive index, due to the electronic interactions of the beam ions with the crystal. In the second step, a saturation of the color centers on the surface is observed together with the appearing of nuclear interactions, reducing the density of the material and of the refractive index. In the last step, a volume saturation take place which lead to an increasing of refractive index in the volume when we have a positive variation of refractive index, compared with the surface of the crystal [3,4,5].

Together with classical color centers (CC's) known as F, F_2, F_3^+, F_3 and F_4, a lot of small F aggregates centers appears during irradiation, which could lead finally to metallic colloids of lithium by successively transformation of Li^+ ions in Li atoms and, due to a thermal effects (even at room temperature) into metallic nanoparticles.

The aim of this paper is a better understanding of the phenomena which take place in ion-implanted LiF crystals with He^+ ions at high energy and different fluencies by optical absorption and emission measurements after irradiation and some thermal treatments.

2. Experimental

Small pieces of LiF crystals, with 10x5x5 mm, where ion-implanted with He^+ high energy particles. The energy of He^+ particles was set at 1.4 MeV and the fluency cover a wide range, starting from 6×10^{13} ions/cm^2 up to 10^{16} ions/cm^2.

One sample was specially prepared with a mask which allows the irradiation in three different zones with three fluencies, between 10^{15} ions/cm^2 to 10^{16} ions/cm^2.

The absorption measurements were performed with a Carry 17 D spectrophotometer and the luminescence measurements were studied part with a Jobin-Yvon spectrofluorimeter and part with the Ar^+ laser excitation and a coupled monochromator-detector device, with a configuration at 45 degree.All measurements were performed at room temperature. The intensities of the color centers luminescence were studied versus the power of the laser between 100 mW up to 400 mW.

To see the fluorescence of color centers, a coupled microscope-photo camera device was used in order to put in evidence the decreasing of the luminescence in the high irradiated zones of the sample.

3. Results

Fig. 1 present the absorption spectra of two irradiated zones at different doses 10^{15} and 10^{16} ions/cm^2. It could be seen a decreasing of the intensities of F and M bands on the high irradiated zone together with an increasing of 420 nm band. This fact could be explained by the well known stages of irradiation: i) at low doses, an increasing of the color centers take place on the surface of the CC's density together with an increasing of the refractive index of the crystals; ii) at medium doses a saturation effect of F and M centers appear together with the increasing of the 420 nm band; iii) at high doses, an small increasing of all bands are observed due to the volume saturation.

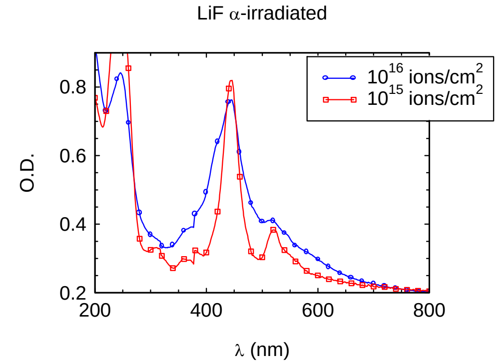

Fig. 1. Absorption spectra on two irradiated zones at different fluencies.

Deconvolution of the spectrum between 400 and 500 nm in the zone high irradiated (fig. 2) exhibits three well resolved peaks at 420 nm, 444 nm and around 460 nm. The peak of 444 nm is well known M center absorption band.

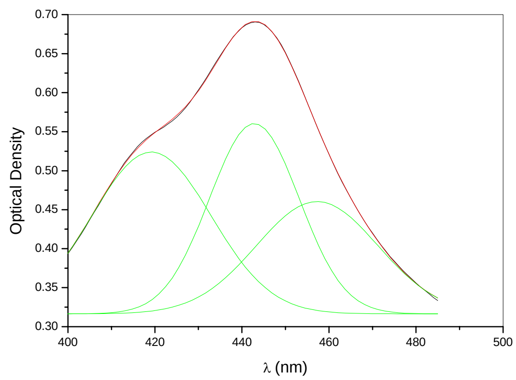

Fig. 2. Deconvolution of the absorption spectrum at high irradiated zone.

It is important to note that the increasing of the 420 nm band is connected with the fluence of beam and not with the energy of the incident ions. In [9] V. Mussi presents interesting absorption spectra at different energies and fluencies. From those spectra, it is very clear that not the energy is important for the appearance of colloidal band but also the dose of irradiation. For example, at 2 MeV energy but 6×10^{13} ions/cm^2, we have no colloidal band but for 1.5 MeV and 5×10^{15} ions/cm^2, this band is very clear.

For the electron irradiated samples, the process of increasing of colloidal band during the time, suggests also a process of aggregation specific for alkali colloids in alkali halide crystals.

The emission spectra of the three irradiated zones show different behaviors (Fig. 3). Firstly, the emissions are drastically reduced in the two more irradiated zones and, secondly, the spectra at high irradiated zone presents more irregularities compared with the spectra of the zone less irradiated.

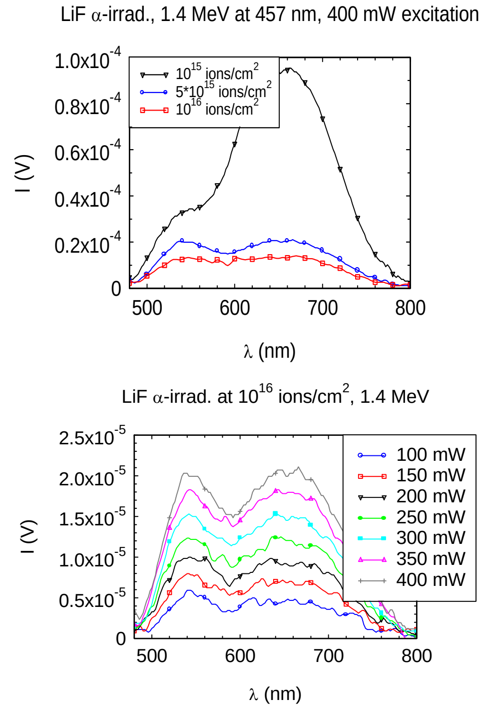

Fig. 3. Emission spectra of ion-implanted LiF crystals.

The deconvolution of the emission spectra on two well known peaks of F_3^+ and F_2 centers versus power of excitation (Fig. 4) exhibits different behaviors.

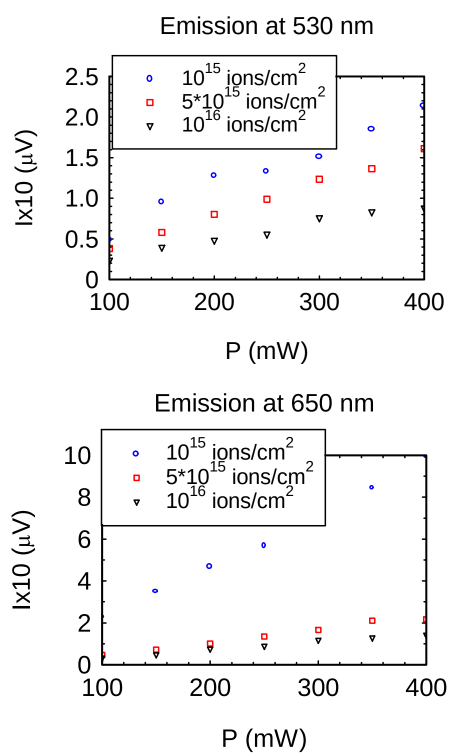

Fig. 4. Emission intensities versus power of excitation.

It is quite clear that the emission of F_3^+ centers is less affected by the presence of 420 nm band, compared with the emission intensities of F_2 centers. This fact, together with the irregularities presented in the emission spectra of high irradiated zone, suggests a scattering of incident light on some small particles.

The annealing of the sample at around 350^0 C, shifts the absorption band from 420 nm to 435-445 nm (Fig. 5). It is important to note that after annealing the sample remain brown colored when the M band disappears. This fact is proved by the drastically decreasing of the emission on high irradiated zone.

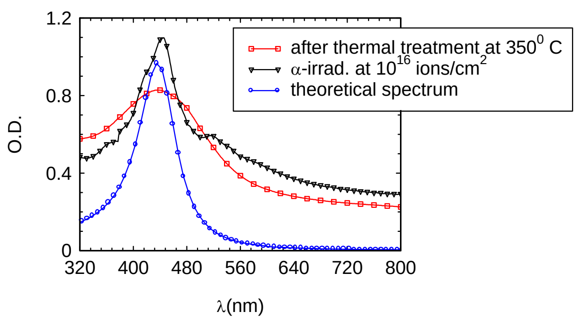

Fig. 5. Absorption spectra before and after annealing.

The annealed sample shows no shift of the band situated at 435 nm with temperature in the range 15-300 K. An image of those three zones under 458 nm excitation is presented in the Fig. 6.

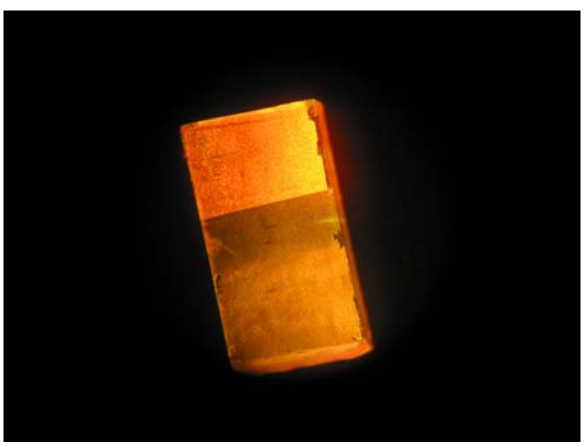

Fig. 6. The image of the irradiated sample with three different zones.

4. Discussion

At high fluency of irradiation, the absorption spectrum is different from the absorption spectrum obtained at low fluency, especially in the zone of F_2 and F_3^+ absorption band. The band from 420 nm could be associated with the formation of lithium metallic colloids at the end tracks of He^+ ions implanted in the crystal. It is not a surprise because the coloration of LiF crystals with 56 MeV He^+ particles induces an absorption band at 425 nm which is shifted at 435 nm after a thermal treatment at around 350 ^oC.

Theoretical calculation of the light scattering on the metallic colloids is based on the Mie theory, which connects the absorption coefficient with the dielectric functions of the metal, which varies with the wavelength of the light:

$$K[mm^{-1}] = \frac{18\pi NV}{\lambda} n_o \frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_o)^2 + {\varepsilon_2}^2}$$

The dielectric constants ε_1 and ε_2 are connected with the wavelength of the light scattering and with the dimension of the colloids [6]

The band from around 460 nm is associated with the large clusters of metallic Li colloids because this band is very clear also in the case of LiF crystals, irradiated with low energy electrons, the penetration of the electrons being practically stopped very close at the crystal surface [6].

Similar features appears in the LiF samples irradiated with H^+ particles with 1 MeV energy, Abbu-Hassan et al. [3] which observe a band at 420 nm when the samples were irradiated with the fluencies over 5×10^{14} ions/cm^2. The authors observed also a large absorption band at 477 nm which appear together with the absorption band peaked at 420 nm. The metallic Li colloids appear also in the case of LiF irradiated crystals with very high energy particles (GeV). K. Schwartz et al. [7] present absorption spectra of LiF crystals, irradiated with Bi^+ at two fluencies. At high fluency a shoulder of M band appear at 420 nm, but no remarks about the presence of this new band are presented in this paper.

A thermal treatment of the samples containing metallic particles on the surface at the temperatures over 180^0 produces a decreasing of the band from 460 nm, because of the evaporation of the metallic lithium.

Beuneu et al. [7] suggest the presence of metallic precipitates after high energy electron irradiation, which depends on the beam flux and fluency. When the flux is high enough, an intense and narrow band appear in ESR measurements, which disappear by annealing of the sample at 300 ^oC. During the isochronal annealing, at low temperatures, the colloids begin to merge, followed by a rapid process of dissolution at high temperatures.

R. A. Wood et al [8] consider the appearance of the band at 414 nm as a splitting of the M band after 30 min. of annealing of the sample at 150 ^oC when the samples were irradiated with 1.5 MeV protons at 10^{15} ions/cm^2 at liquid nitrogen temperature.

In order to fit the transmission spectra of ion-implanted LiF samples, Montecchi et al. [9] take into account a band at 416 nm which tentatively was attributed to nanoaggregates of Li.

5. Conclusions

Irradiation with He^+ particles of 1.5 MeV at fluencies over 5×10^{15} ions/cm^2 leads to the appearance of two absorption bands at 420 and 460 nm. The first one appears probably due to the metallic colloids in the crystal, the second one being due to the metallic lithium islands which are formed on the surface of the sample as a saturation effect of (F, F_n) centers during the irradiation process.

Annealing of the sample over the melting point of metallic Li (around 180 ^oC) leads to an increasing of the colloids from the bulk, part of Li atoms continuous the nucleation process in the bulk. This fact is demonstrated by the shift of the band from 420 nm to 435-445 nm after thermal treatment. When the temperature is high enough (over 180 ^oC) an evaporation process from the surface take place, reducing the absorption from 460 nm.

The metallic islands obtained after annealing have large dimensions due to a liquid-like coalescence process in which the enlargement take place in the liquid phase of the lithium. The phenomenon is similar with that observed in the case of indium colloids [10]

The estimated dimensions of the colloids are obtained using Mie theory program with the following constants: plasma frequency 6.73 eV, damping constant 5.81×10^{-15} s, Fermi velocity 1.28×10^{28} m/s. The dependence of the wavelength of the optical constants from Li was taken from [11]. It is clear that the band at 420 nm is due to the absorption effects on small metallic particles having an estimated radius of about 10 nm. For the peak position at 435 nm the high order of scattering of light appears, the peak remaining in the same position between 15-300 K temperatures, but an estimated radius seems to be 35 nm. For the peak position at 460 nm, the metallic particles are too large to apply the Mie theory, but a roughly approximation gives a dimension around 140 nm, in agreement with the conclusions of Beuneu et al.[7].

The reduction of the F_2 and F_3^+ emissions is due to the overlap between the M absorption band and the colloidal one. The decrease of the M band together with the increase of the intensity of the 420 nm band versus irradiation doses, suggest a transformation of those centers in small F_n-aggregates during the irradiation process, followed by a metallic conversion of Li ions.

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